Theory of behavior of ionized hydrogen in GaSb crystal structure

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ABSTRACT

Using the thermodynamical studies it seems proved that ionized hydrogen acts as amphoteric dopant of GaSb. It is splitting to H^+ (acceptor) and H^- (donor) and between these two kinds certain equilibrium is created depending on the concentration of acceptor's and donor's impurities in the GaSb material. There is an inclination of such a crystal to maintain the GaSb structure to be isoelectric. This behavior has been studied on undoped and slightly Te-doped GaSb single crystals grown by use of the Czochralski method without encapsulant under a flow of ionized hydrogen. For comparison the studies were repeated under a flow of molecular hydrogen.

Keywords: ionized hydrogen, GaSb crystal structure, residual acceptors, free carrier concentration.

1. INTRODUCTION

Systematic work lasting for more than three decades has been devoted mainly to the role of residual concentration of natural acceptors which is a limiting factor of the device application of gallium antimonide (GaSb)[1]. The residual acceptors of the concentration of about 1.7 x 10^{17} cm^{-3} were identified as vacancy (V) complexes $V_{Ga}Ga_{Sb}$[2,3]. Many attempts have been made to reduce their content in GaSb. Crystal growth from the nonstoichiometric melt[4] was one of the most successful methods. This result supported our interest in opening the question of the GaSb single crystal growth from the melt with a reduced content of residual acceptors.

Hydrogen passivation of different defects and impurities was studied in many III-V compounds[5,6]. Polyakov et al.[7,8] treated GaSb samples either undoped or Zn- or Si-doped both in hydrogen and deuterium atmosphere in the temperature range between 100 and 250°C and with the exposure times of 0.5 - 1 h. Their results were very interesting. The carrier concentration in the case of undoped GaSb decreased as much as to the value of about 1 x 10^{16} cm^{-3} and the resistivity increased by one order of magnitude.

Polyakov et al.'s method showed that this way was likely to successfully manage the preparation of at least high-resistivity GaSb single crystals with a low concentration of residual acceptors.

We tried to use our undoped GaSb single crystal (grown in molecular hydrogen atmosphere) having a carrier concentration of (1.70 - 1.80) x 10^{17} cm^{-3} and a resistivity of (6.50 - 6.70) x 10^{-2} Ω.cm. The wafer from this crystal were cut to a thickness of 200 μm. The samples were treated in a quartz tube at temperatures of 350, 280, 250, 200 and 150°C for 1 - 24 h. Hydrogen ionized by means of a deuterium lamp flew through this annealing reactor. After cooling the quartz ampoule, the carrier concentration and the resistivity were measured on the treated wafers in the first step using the van der Pauw method. Then the layers of about 10 μm on both sides of the wafers were ground out and the electrical measurements were repeated.

It turned out that in the case of the temperature range of 250 - 350°C, the values of the measured parameters were the same, both before the temperature annealing and after this treatment. However, when the temperature was lower, i.e. from 200°C and mainly 150°C, and the duration of the annealing procedure exceeded 10 h, the carrier concentration in the nonground wafers achieved the value of (1.20 - 1.30) x 10^{17} cm^{-3} (i.e. about 40%). After grinding a 10 μm layer, the carrier concentration was the same as in the case of the untreated samples. The resistivity changed only by 15%; i.e. it reached the values of (7.60 - 7.70) · 10^{-2} Ω·cm.

This method of measurement is influenced by a high inaccuracy because the total volume of the samples was measured while only a small layer was passivated. For this reason, the resistivity and the free carrier concentration were

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studied by the spreading resistivity procedure. It has been found that in the case of the wafers being treated at a temperature of 150°C for 24 h, the thickness of the passivated layer was only 0.4 - 0.6 μm and its resistivity reached a value of 10^2 - 10^3 Ω.cm. The free carrier concentration was lower than 1 x 10^{15} cm^{-3}. However, such a thin layer of high-resistivity GaSb single crystals would be difficult to fabricate because, on the one hand, the thickness of the layer was not uniform on the surface of the wafer and, on the other hand, the spreading of the resistivity was very inhomogeneous.

2. EXPERIMENTAL

For the reason mentioned above, we tried to prepare bulk crystal in such an atmosphere that would make possible to study the influence and stableness of ionized hydrogen flow on free carrier concentration and resistivity of as-grown single crystals. The GaSb crystals were grown in our laboratory using the Czochralski method without encapsulant under the hydrogen atmosphere that suppressed the creation of an oxide scum on the melt surface[9]. A polycrystalline material made by the firm Spurmetalle Freiburg (Germany) was used as the starting material for our investigation. Before the growth, the polycrystalline GaSb was cleaned by grinding and etching in a solution of acids (6 HNO_3 + 2 HF + 1 CH_3COOH) followed by distilled water rinses, and then placed in a quartz crucible. For the reason of evaporation of antimony during the whole growth process, a small amount of antimony (0.1 wt.%) was added into the melt to prevent the non-stoichiometric growth of crystals. It was found that about 1x10^{-3} mol of antimony could be lost in gas form from the apparatus owing to the flowing hydrogen atmosphere[10]. Dopant (tellurium) was used in an elementary form and was added during the preparation of the polycrystalline material. The apparatus with the starting material was closed and rinsed out by very pure hydrogen during 24 hours in order to removing oxygen. From a very good quality undoped GaSb single crystal, the seed was cut at a length of about 5 cm having the dimensions 4 mm x 4 mm with an orientation of <111>b (Sb) to the melt.

The axial temperature gradients close to the solidification interface were about 35 $grad.cm^{-1}$, that is very low in comparison with other methods; for example, with the liquid encapsulated Czochralski (LEC) they reached up to 200 $grad.cm^{-1}$. The horizontal gradient on the solid/liquid interface was almost flat. The pulling rate was 12 $mm.h^{-1}$ with a rotation of the seed of about 20 - 25 rpm.

During the crystal growth two different kinds of atmosphere were used:

a) very pure "atomic" hydrogen (ionized by deuterium lamp)
b) very pure "molecular" hydrogen (for comparison)

The length of these crystals was about 60 mm and a diameter of about 20 - 25 mm.

For the investigation of electrical properties and dislocation density the GaSb crystals were cut along the growth direction to prepare samples of about ~ 1 mm thick. Both faces of wafers were mechanically polished using an alumina suspension on a thick glass plate. Afterwards the wafers were rinsed in water, in acetone and finally in distilled water several times. The free carrier concentration, mobility and resistivity of each crystal were measured using the van der Pauw method at room temperature, with an accuracy of about ±8%.

3. RESULTS AND DISCUSSION

The crystals were grown from the same starting material containing always the same residual impurities. Undoped crystals grown under the molecular hydrogen atmosphere showed the starting carrier concentration (in the top part of crystals) of 1.7 x 10^{17} cm^{-3}. This concentration along the growth direction has decreased down to 0.8 x 10^{17} cm^{-3}. This effect is caused by the increasing concentration of the n-type impurities in the starting melt because their distribution coefficients are lower than 1. The concentration of n-type impurities in our material was higher than the concentration of p-type elements and therefore during the growth, the compensation of natural acceptors occurred[2].

It appears from these measurements, that the growth under ionized hydrogen atmosphere influences the electrical behavior of GaSb. However, the certain asymmetry in acceptor and donor passivation in GaSb material appears. In comparison with Polyakov's opinion[7] we assume that the passivation of donors is higher than the passivation of acceptors, what should be confirmed in increasing of resistivity and of almost the same value of the free carrier concentration. For this reason we tried to prepare GaSb single crystals lightly doped with tellurium (3.12 x 10^{17} $atoms.cm^{-3}$).

The concentration of tellurium in the top parts of crystals, calculated using the Pfann equation, shows the value of 1.0 x 10^{17} atoms.cm^{-3} and consequently the free carriers concentration is theoretically 0.7 x 10^{17} cm^{-3} (p-type). It is necessary to notice that the crystals were always pulled up so far that no melt was remaining any, i.e. up to x = 1 (x is the solidifying fraction). The bottom part (0.98 > x > 1) of crystals is always cut off. Thus, the crystals are ready to the measurements in the range of 0 < x < 0.98. According to our previous studies of the GaSb crystals grown under molecular hydrogen atmosphere[2], the bottom fraction (x = 0.98) has showed that the tellurium concentration was about (3.5 - 4.5) x 10^{17} atoms.cm^{-3}, i.e. these parts of the crystals were always n-type with the free carriers concentration of the value of (1.8 - 2.8) x 10^{17} cm^{-3} (the starting concentration of tellurium in the melt was also 3.12 x 10^{17} atoms.cm^{-3}). However, the GaSb crystals doped with tellurium (the starting concentration of tellurium in the melt was the same, 3.12 x 10^{17} atoms.cm^{-3}) grown under the ionized hydrogen atmosphere showed quite different electrical properties from crystals pulled under the molecular hydrogen atmosphere. The free carrier concentration at the top of a crystal was 1.79 x 10^{16} cm^{-3} and resistivity 0.951 Ω.cm and at the end of the crystal 2.26 x 10^{16} cm^{-3}and 0.705 Ω.cm. The whole crystal bowl showed p-type conductivity.

It is worth mentioning that the values of the free carrier concentration and resistivity were almost the same in a whole crystal in both directions, i.e. in the longitudinal and transversal directions to the growth axis. The homogeneity of the electrical properties was surprisingly quite good.

Electrical results show different values in both cases of used atmosphere (molecular and ionized hydrogen). According to the thermodynamical studies and calculations of the distribution of free carrier concentration in GaSb crystals, we prepared two figures that could very well describe behavior of ionized hydrogen in GaSb structure (see Fig.1. and Fig.2.).

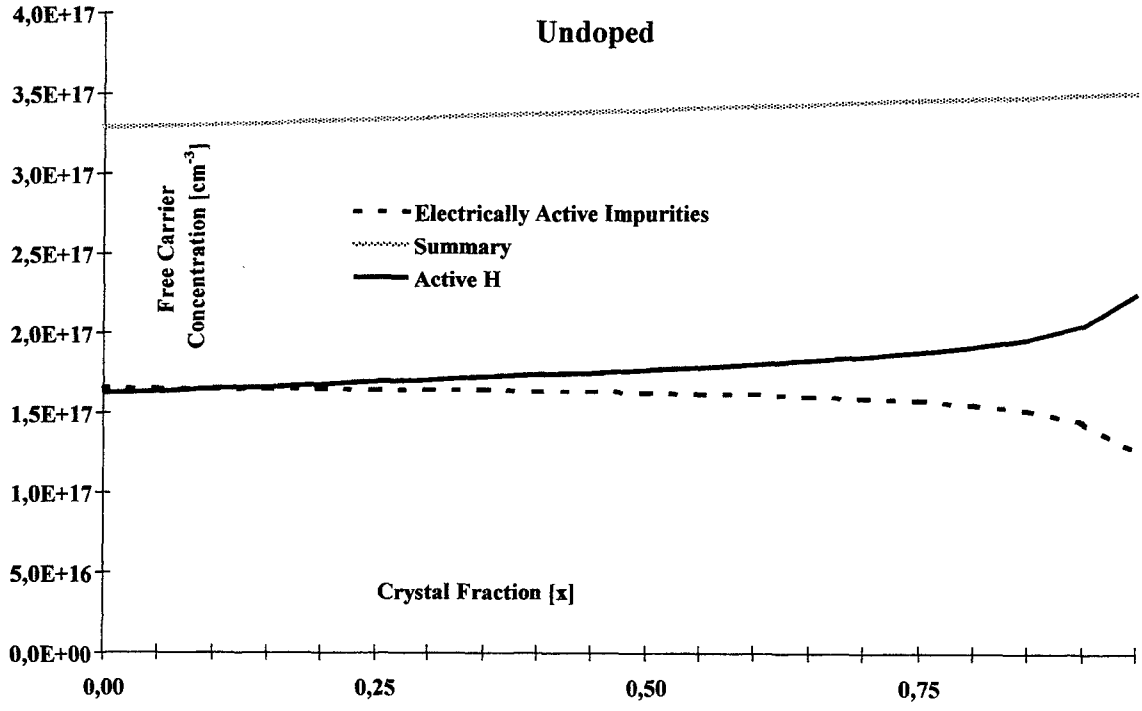

Fig. 1. Free carrier concentration distribution along to the growth axis in undoped GaSb single crystals grown using the Czochralski method in molecular and ionized hydrogen atmosphere.

As one can see on the figures 1 and 2, the concentration profiles of free carriers along the growth axis of the crystals grown in ionized hydrogen atmosphere (IHA crystals) are different in comparison with the profiles of the crystals

grown in molecular hydrogen atmosphere (MHA crystals). While MHA crystal profiles have logarithmic shape and could be very well described by Pfann equation, the IHA crystal profiles are almost exacting linear. It is visible for undoped and also for Te-doped GaSb. In the case of MHA crystals, the free carrier concentration has a decreasing tendency because the concentration of donors increases (it is also valid for undoped GaSb because the concentration of n-type impurities is higher than p-type ones in the starting GaSb material). However, IHA undoped and low Te-doped crystals have a slightly increasing profile. We follow our theory suggesting the preferably passivation of donors than acceptors.

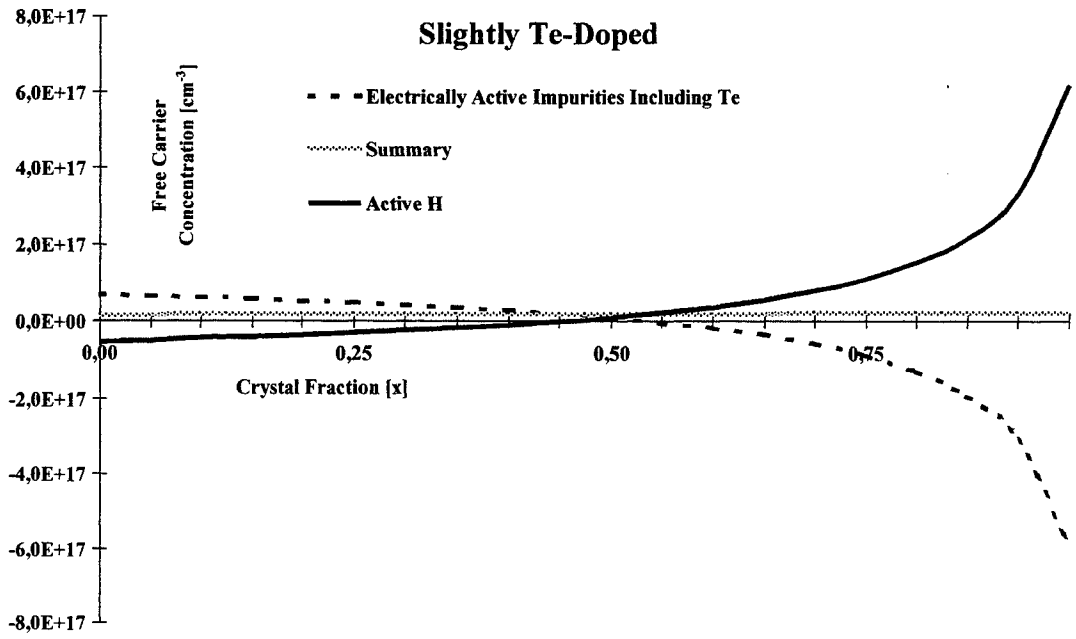

Fig. 2. Free carrier concentration distribution along to the growth axis in slightly Te-doped GaSb single crystals grown using the Czochralski method in molecular and ionized hydrogen atmosphere.

While molecular hydrogen during the growth procedure acts as an electrically neutral component and only reduces present oxides (Ga_2O_3, etc.) and surplus oxygen, ionized hydrogen could be taken into consideration as an electrically active element. For this assumption the fact gives evidence that atomic gases always show higher activity in principle than molecular ones do. However, ionized hydrogen could be split to two different so-called dopants - acceptors as H^+ and donors as H^-. According to the free carrier concentration profiles along the crystal growth axis we assume an explanation that ionized hydrogen in GaSb is mainly an acceptor with a level close to the valence band edge. Calculating theoretically the active concentration of H^+ in crystals by using the Pfann equation, the distribution coefficient could be k_{eff} = 0.15 and than in the case of undoped GaSb crystals, the resulting free carrier concentration profile is a summary of the active concentration of impurities in the starting GaSb material and of the increasing concentration of H^+. Seeing free carrier concentration profiles in slightly Te-doped GaSb, it seems that the behavior of ionized hydrogen is different. However, these results give us more detailed explanation how active hydrogen acts in GaSb structure.

Ionized hydrogen is split to H^+ and H^- active "dopants" which act as acceptors and/or donors. Between these two kinds certain equilibrium could be created in dependence on the concentration of acceptor's and donor's impurities in the GaSb material. There is an inclination in such a crystal to maintain the GaSb structure to be isoelectric. The suggested effect can be described by the following equations:

$$[H^+] \approx C_n \quad \text{and} \quad [H^-] \approx C_p \quad \text{, or} \qquad (1)$$

$$k_1 \cdot \frac{[H^+]}{[H^-]} \approx k_2 \cdot \frac{C_n}{C_p} \quad \text{, while} \tag{2}$$

$$[H^+] + [H^-] = K_H \tag{3}$$

where C_p and C_n are acceptor's, resp. donor's concentration, and k_1 and k_2 are constants. K_H is a maximal concentration of ionized hydrogen in GaSb structure and reaches a value[7] about of 10^{17} - 10^{18} atoms.cm^{-3}. The ionized hydrogen seems to be an amphoteric material such as silicon. Concentration of H^+ increases with the concentration of donors, and vice versa, however, this splitting of active hydrogen to H^+ and H^+ is limited by its total concentration.

The mathematical evaluation of this equilibrium should be next step of our study using thermodynamical methods to be able to effectively decrease free carrier concentration and to increase resistivity of GaSb single crystals.

4. CONCLUSION

The growth of GaSb single crystals under a flow of ionized hydrogen leads to lower free carrier concentration because of passivation of residual impurities (including dopants) and/ /or structural defects. It seems that the incorporated ionized hydrogen is splitting to H^+ and H^- active agents that could be characterized as acceptors and donors. Their concentrations depend on content of acceptor's and donor's dopants (impurities, structural defects, etc.) in the GaSb crystals. For a satisfactory growth of crystals with the free carrier concentration lower than 10^{15} cm^{-3} (which is the desired goal of scientists working with GaSb substrates) it is necessary to deal with a whole series of crystals with various concentrations of tellurium in the starting melt. According to our preliminary calculation, the optimal concentration should be (6 - 8) 10^{17} atoms.cm^{-3} of tellurium and such prepared crystals should show the free carrier concentration of about 10^{14} cm^{-3} along the whole crystal bowl. However, the total concentration of incorporated ionized hydrogen could be equivalent to the concentration of the whole impurities in GaSb material.

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REFERENCES

1. H.Welker, "Über neue halbleitende Verbindungen II," *Z.Naturforsch.* **8a**, pp. 248-251, 1953.
2. B.Štěpánek and V.Šestáková, "Czochralski grown concentration profiles in the undoped and Te-doped GaSb single crystals," *Thermochim. Acta* **209**, pp. 285-294, 1992.
3. Y.J.Van der Meulen, "Growth properties of GaSb: The structure of the residual acceptor centers," *J.Phys.Chem.Solids* **28**, pp. 25-32, 1967.
4. D.Effer and P.J.Etter, "Growth of GaSb from non-stochiometric melt," *J.Phys.Chem.Solids* **25**, pp. 451-460, 1964.
5. S.J.Pearton, J.W.Corbett and T.S.Shi, "Hydrogen in crystalline semiconductors," *Appl.Phys.* **A 43**, pp. 153-195, 1987.
6. J.Chevallier and M.Aucouturier, "Influence of hydrogen atmosphere in III-V semiconductor crystals," *Ann.Rev.Mater.Sci.* **18**, pp. 219-268, 1988.
7. A.Y.Polyakov, S.J.Pearton, R.G.Wilson, R.Rai-Choudhury, R.J.Hillard, X.J.Bao, M.Stam, A.G.Milnes, T.E.Schlesinger and J.Lopata, "Hydrogen treatment effect on shallow and deep centers in GaSb," *Appl.Phys.Lett.* **60** , pp. 1318-1320, 1992.
8. A.Y.Polyakov, M.Stam, A.G.Milnes, R.G.Wilson, Z.Q.Fang, P.Rai-Choudhury and R.J.Hillard, "High-resistivity GaSb grown by molecular-beam epitaxy," *J.Appl.Phys.* **72**, pp. 1316-1319, 1992.
9. V.Šestáková, B.Štěpánek, J.J.Mareš and J.Šesták, "Decrease in free carrier concentration in GaSb crystals using an ionized hydrogen atmosphere," *Materials Chemistry and Physics* **45**, pp. 39-42, 1996.
10. F.Moravec, V.Šestáková, B.Štěpánek and V.Charvát, "Crystal growth and dislocation structure of gallium antimonide," *Cryst.Res. Technol,* **24**, pp. 275-281, 1989.